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Radical polymerization of Biphenyltetrazonium Complex Salt within DMF and Alkaline Solution

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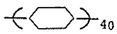
Abstact

The authors found that biphenyltetrazonium complex salt made from biphenyltetrazonium chloride (BTC) and cuprous chloride was polymerized within DMF and the like organic solvents and also concentrated alkaline solutions, thus obtained products were easily soluble in benzene and DMF, further a component of about  was generated. On the other hand, a polyphenyl was produced by A. A. Berlin, addng Cu^{+} + NH_4OH within aqueous BTC and most of the products were scarcely soluble in organic solvents.

Then in order to compare these two polymerization methods, the materials of 1) BTC, 2) BTC - double salt, 3) BTC - complex salt, were prepared and individually acted on within organic and inorganie agents. Polymerizations by the extraction of cupric chloride toward complex salt and that of chlorine toward BTC and double salt were confirmed by mean of pH decrease within acting liquors and detection of cupric chloride and chlorine.

A fractionated component of the former is soluble in organic solvents and scarcely soluble that of the latter. The former is mainly combined at 4 and 4′ position of biphenyl and the latter is assumed to have a complicated structure by mean of IR spctrum.

1 Introduction

It was previously reported by A. A. Berlin that a poly-phenyl was synthesized by adding Cu^{+} + NH_4OH within aqueous biphenyltetrazonium chloride and most of the pro-ducts were scarcely soluble in organic solvents.[1] The authors carried out the same reaction, using Fe^{2+}, Sn^{2+} and Ti^{3+} besides Cu^{+}, as an initiator, but results obtained were the same.

On the other hand, the authors found tbat biphenyletrazonium complex salt made from biphenyltetrazonium chloride (to be referred to as BTC) and cuprous chloride was polymerized within DMF and the like organic solvents and also concentrated alkaline solutions, and thus obtained products were easily soluble in many solvents such as benzene and DMF, and further, a component of about $\left(-C_6H_4-\right)_{40}$ was generated,

Then, in order to clarify the difference between these two polymerization mechanisms, the materials of 1) BTC, 2) BTC-Cu_2Cl_2 or $Zncl_2$ double salt, 3) BTC-Cu_2Cl_2 complex salt were prepared and individually acted on within organic and inorganic agents, and characteristics of the products were investigated.

2 Experimental

2.1 Preparation of materials

2.1.1 BTC : Tetrazotization was carried out by dropping aqueous sodium nitrite (14g/30cc water) at 7 – 10°C within a mixture in which 13g of benzidine hydrochloric acid, 15cc of 35% hydrochloric acid and 15cc of water were well kneaded and cooled. Total solution of sodium nitrite (twice of the calculated) was continuously dropped after the end of tetrazotization. A yellow crystal was salted out while leaving at 0°C overnight.

2.1.2. BTC – Cu_2Cl_2 complex salt; Dropping at 5 – 10°C, 40cc of 35% hydrochloric acid dissolved 11g of cuprous chloride within 100cc of aqueous solution dissloved 14g of BTC and 14g of sodium nitrite, a brown precipitate was obtained.

2.1.3. BTC – Cu_2Cl_2 double salt : The above procedure was carried out below – 5°C, and when a large excess of cold acetone was added in this green solution, a yellowish-green precipitate was obtained.

2.1.4. BTC - $ZnCl_2$, $CuCl_2$ double salt : A yellow precipitate was obtained by adding hydrochloric acid solution dissolved zinc chloride or cupric chloride at 5 – 10°C into the aqueous BTC.

2.2 Polymerization

Polymerization was carried out according to the combination of Table 1. A used agent was DMF, DMSO, THF and pyridine (organic) and $NaOH$,Na_2CO_3 and NH_4OH (alkali) and a solution of NH_4OH dissolved

Table 1 Reaction condition and solubility of the products

Agent / Materials	D M F	Alkali	$Cu^{+} + NH_4OH$
B T C	×	B	B
Double salt	×	B	B
Complex salt	A	A	A

× : No polymerized
A : Soluble in organic solvents B : Insoluble

Cu_2Cl_2. The end of reaction was indicated by the termination of bubbling. After washing enough with water, the product was filtered and dried.

2.3. Fractional precipitation

The products were put into cylindrical filter paper and a low molecular weight component was extracted with methanol utilizing the Soxhlet extractor and thereafter with benzene. The products made from complex salt was almost soluble in benzene, then the fractional precipitation was carried out by adding a small amount of petroleum benzine into this benzene solution under agitation.

2.4 Elemetal analysis and molecular weight measurement

Elemental anaysis was carried out utilizing CHN Corder. Molecular weight was measured by VPO method with benzene solution. IR spectrum was examined by KBr tablet method.

3 Results and discussion

3.1 Characteristics of materials

Figure 1 shows the IR spectrums of BTC, its double salt and complex salt. Absorption of $-N{\equiv}N$ observed at 2275cm^{-1} on those of BTC and double salt shifts at 2230 cm^{-1} in case of complex salt, but yet its existence is surely confirmed. Therefore, it can be said that $-N^{+}{\equiv}N.Cl^{-}$ and $Cu^{+}Cl^{-}$ inside the complex salt can not independently behave, because they are coordinated with strong interaction force and lose their ionic character.(2)

A shift of the characteristic absorption between benzenediazonium double salt and complex salt is the same as the above.

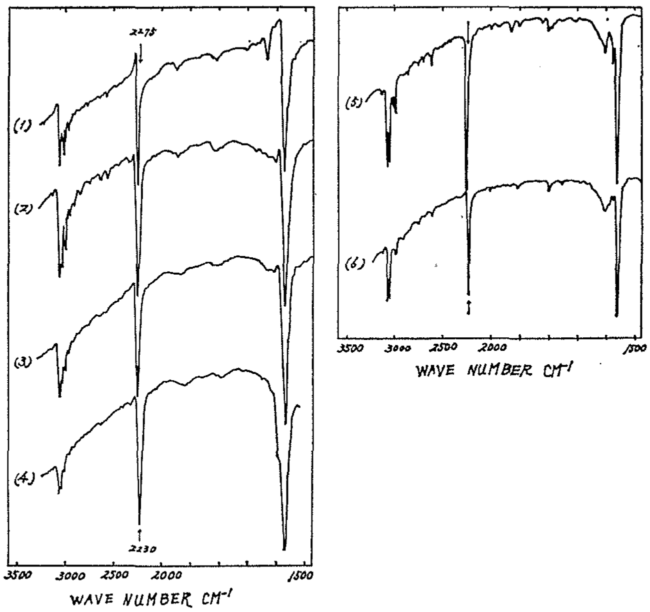


Fig. 1 IR spectrum of materials (KBr tablet method)

(1) BTC

(2) 〃 $-ZnCl_2$ double salt

(3) 〃 $-Cu_2Cl_2$ 〃 〃

(4) 〃 $-Cu_2Cl_2$ complex salt

(5) BDC $-Zn_2Cl_2$ double salt

(6) 〃 $-Cu_2Cl_2$ complex salt

BDC : Benzenediazonium chloride

Table 2 Characteristics of materials

Materials	Color	Constitution (elemental analysis)	Activity	
			coloring[a]	heating
B T C	yellow	ClN_2—⬡—⬡—N_2 Cl	+ +	explode[c]
BTC-$ZnCl_2$ (D.S.)	〃	(—⬡— $N_2Cl)_2ZnCl_2$	+ +	〃
〃 -$CuCl_2$ (D.S.)	〃	(—⬡— $N_2Cl)_2CuCl_2$	+ +	〃
〃 -Cu_2Cl_2 (D.S.)	yellowish green	(—⬡— $N_2Cl)_2Cu_2Cl_2$	+ +	〃
〃 -Cu_2Cl_2 (D.S.)	brown	(—⬡—⬡— $N_2Cl)_2Cu_2Cl_2$[b]	+	melt[d]
BDC-$ZnCl_2$ (D.S.)	white	⬡— $N_2Cl\,{}^1/_2\,ZnCl_2$	+ +	explod
〃 -Cu_2Cl_2 (C.S.)	brown		+	black fluid

a) : Diazocoupling within aqueous β-naphthol'
b) : The form of dimer
c) : 125 °C
d) : polymerized (D.S.) : Double salt, (C.S.) : Complex salt, BDC : Benzenediazonium salt

Table 2 shows the characteristics of materials. BTC and double salt have almost a same character, namely they explode at 125°C and partly dissolve in water and β-naphthol is diazocoupled within this solution. Contrary to this, complex salt melts above 105°C and becomes a black fluid and the coloring by diazocoupling is weak, due to few dissolution within water. Radical polymerization takes place only by heating the complex salt.

Table 3 shows the activity of organic solvents toward the materials

Table 3 Activity within organic solvents

Materials	D M F	DMSO	pyridine	T H F	Methanol	Aceton	Dioxane	Benzene
B T C	−	−	−	−	−	−	−	−
BTC−$ZnCl_2$ (D.S.)	−	−	−	−	−	−	−	−
〃 −$CuCl_2$ (D.S.)	−	+	+	−	−	−	−	−
〃 −Cu_2Cl_2 (D.S.)	+	+	+	−	−	−	−	−
〃 −Cu_2Cl_2 (C.S.)	+++ ※	+++ ※	+++ ※	+++ ※	+	−	−	−
BDC−$ZnCl_2$ (D.S.)	−	−	−	−	−	−	−	−
〃 −Cu_2Cl_2 (C.S.)	+++	+++	+++	+++	+	+	+	−

with a measure of bubbling degree. Both BTC and double salt generally show no changes within organic solvents and no polymerized product can be generated even when a few bubbling is observed with some materials. Complex salt is acted on with DMF, DMSO, THF and pyridine following hard bubbling and color of the solution changes in dark brown. These solvents are good solvent of polymerized substances and have also a dissolution power toward cupric chloride anhydride.

3.2. Reaction mechanism between complex salt and DMF

DMF dissolves slightly BTC and double salt following the yellowing and few bubbling and no polymerization. But β-naphthol is diazocoupled with this solution following remarkable coloring. Complex salt is polymerized within DMF following hard bubbling and the same is the solution of 10% DMF (by volume) diluted with benzene.

3.2.1. Polymerization mechanism

1) Cupric chloride is generated within DMF in accordance with polymerization. It is confirmed by blueing of the solution when the acting liquor after end of reaction was gently poured into IN aqueous sodium hydroxide.

$$CuCl_2 + 2NaOH \longrightarrow 2NaCl + Cu(OH)_2 \text{ (3)}$$

2) Cuprous chloride does not come off from the complex salt during the reaction. It is not soluble in alkaline solution, but is sunk at the bottom becoming brownish-red precipitate which can not be confirmed on the same examination mentioned above.

$Cu_2Cl_2 + 2NaOH \longrightarrow 2NaCl + 2CuOH$ [3]

3) Cupric chloride is remarkably soluble in DMF uniting by a strong interacting force, then the union loses the activity toward complex salt.

a) DMF solution saturated with cupric chloride and subsequently diluted with benzene is difficult to bubble at room temperature when complex salt is added in this solution.

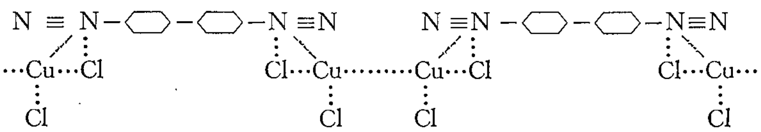
b) It bubbles even at the same temperature when previously heated at 50°C and freed a brown precipitate (color of cupric chloride anhdride).

c) when complex salt is added within a solution in which a small amount of DMF is diluted with benzene, bubbling takes placet temporarily, but it stops at the lack of DMF. And it starts again by supplement of DMF.

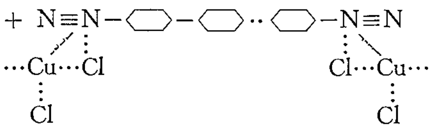
4) $-N^+{\equiv}NCl^-$ and Cu^+Cl^- inside the complex salt are impossible to behave independently because they are coordinated with a strong union force losing the ionic character.

5) Complex salt has more and more shaded color than that of BTC and double salt. Then electron transfer along its conjugated system may be possible. [4]

If the constitution of the complex salt is assumed as (A) founded on 4) and 5), it is confirmed from the fact of 1), 2) and 3) that cupric chloride is extracted from the complex salt by the action of DMF and dissolved with a strong dissolution power following appearance of radical. It is shown in formula (1).


(A)

$(A) + DMF \longrightarrow 2N_2\uparrow + (2CuCl_2 + DMF)$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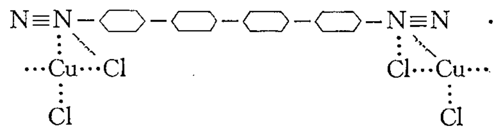
(1) ⟶ 
...... (2)

A pair of radical generated on the opposit sites at 4 and 4′ of biphenyl is at once disappeared by their union and the molecule grows as formula (2).

Accordingly, polymerization of the complex salt within DMF is advanced by repeating reaction between appearance of radicals by formula (1) and its disappearance followed by growth of molecula by formula (2). This polymerization mechanism is quite different from a usual radical polymerization.

3.2.2. Constitution of polymerized products

Table 4 shows the condition of polymerization and characteristics of the fractionated component. A component produced by the reaction at 10°C for 24hr. between complex salt and a mixed solution of benzene and 10% DMF (by volume) and thereafter refined with methanol becomes soluble in benzene and DMF. A fractionated component whose molecular weight is 3300 has a melting point higher than 360°C and its nitrogen content is 5.5%.

When a greater part of nitrogen is evolved generating a phenylradical, a part of it may be left generating an azoradical followed by the union of each radicals. Then if the constitution of the fractionated component is assumed as —(-⌬—⌬-)$_m$—(-⌬—N=N-)$_n$— , a calculation of the relation between m and n at 5.5% of nitrogen gives m = 2n. Then one sixth of nitrogen is left and the constitution of this component is equivalent to (⌬ × 41 + N = N × 7) . When complex salt was acted on within DMSO, THF and pyridine, a extracting reaction of cupric chloride was confirmed. These polomerization mechanism are the same as the case of DMF.

3.3 Polyuerization within alkaline solution

When BTC and double salt are put into alkaline solution (pH10), pH of this solution gradually decreases following hard bubbling. It is shown

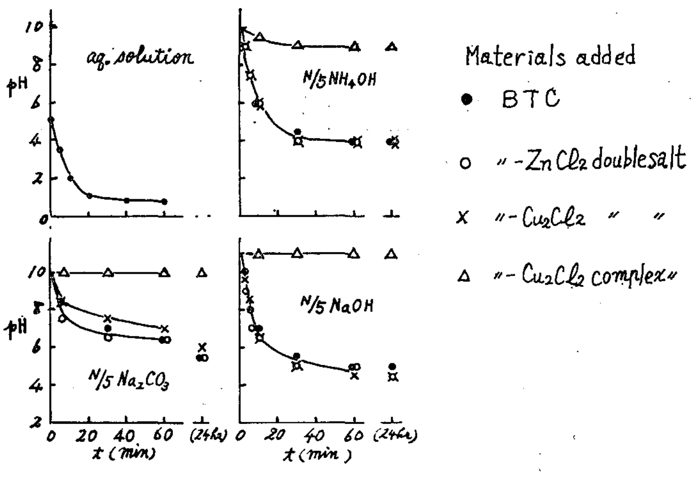


Fig. 2 PH Change in dilute akaline solutions (pH10)

Table 4 Characteristics of the polymerized product

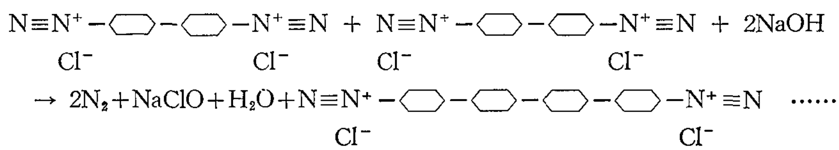
Materials	Reacton condition				Solubility of refined matter a)	
	Reagent		Temp (°C)	Time (hr)	C_6H_6	DMF
B T C Cu_2Cl_2 Complex salt	Oragnic agcnts	D M F 10% / C_6H_6	10	24	○	◎
		〃 5% / C_6H_6	50	50	○	◎
		〃 4% / p.b.	〃	〃	○	◎
		DMSO 10% / C_6H_6	10	24	○	◎
		T H F 10% / C_6H_6	〃	〃	○	◎
		〃 5% / p.b.	50	50	○	◎
		pyridin 10% / C_6H_6	10	24	○	◎
		〃 5% / p.b.	50	50	○	◎
	Alkaline solution	2.7% NH_4OH	30	24	○	◎
		Sat. CH_3COONa	〃	〃	○	◎
		〃	50	〃	○	◎
		10% Na_2CO_3	30	〃	○	◎
		〃	50	〃	○	◎
		10% NaOH	30	〃	○	◎
		〃	50	〃	○	◎
B T C		2.7% NH_4OH	30	〃	×	×
		10% Na_2CO_3	50	〃	×	×
		10% NaOH	〃	〃	×	×
B T C $ZnCl_2$ double salt		2.7% NH_4OH	30	〃	×	×
		Sat. CH_3COONa	50	〃	×	×
		10% Na_2CO_3	〃	〃	×	×
		10% NaOH	〃	〃	×	×
B T C Cu_2Cl_2 double salt		2.7% NH_4OH	30	〃	×	×
		Sat. CH_3COONa	50	〃	×	×
		10% Na_2CO_3	〃	〃	×	×
		10% NaOH	〃	〃	×	×

p. b. : petroleum benzine a) : Refined matter extracting with methanol
b) : Fractional precipitation from benzene solution with petroleum benzine. Solubility; × : Insoluble ○ : Soluble ⊙ : Completely soluble

Characteris of fractionated component b)				
Coloring	Molecular weight	mp (°C)	N (%)	Constituion -(-⬡-⬡-)$_m$-(-⬡-⬡-N=N-)$_n$-
dark brown	3,300	>360	5.5	⬡ × 42 + N = N × 7
〃	2,250	180	4.9	⬡ × 26 + N = N × 4
〃	2,350	220	5.4	⬡ × 26 + N = N × 4
〃	3,500	280	6.1	⬡ × 44 + N = N × 8
light brown	2,000	270	6.6	⬡ × 24 + N = N × 5
〃	1,500	155	5.3	⬡ × 16 + N = N × 3
dark brown	1,550	220	5.6	⬡ × 18 + N = N × 3
brown	1,300	190	6.8	⬡ × 14 + N = N × 3
〃	980	190	7.4	⬡ × 12 + N = N + 3
dark brown	1,800	225	8.1	⬡ × 20 + N = N × 5
〃	2,050	275	5.4	⬡ × 24 + N = N × 4
〃	1,300	210	6.6	⬡ × 14 + N = N × 3
〃	1,500	250	5.3	⬡ × 18 + N = N × 3
〃	1,400	220	7.5	⬡ × 16 + N = N × 4
〃	2,550	>360	7.0	⬡ × 30 + N = N × 6
brown	—	>360	11.9	
〃	—	〃	8.8	
dark brown	—	〃	5.5	
brown	—	〃	10.4	
〃	—	〃	8.4	
〃	—	〃	8.3	
dark brown	—	〃	6.2	
browu	—	〃	9.5	
〃	—	〃	5.3	
〃	—	〃	6.6	
dark brown	—	〃	5.3	

in Figure 2. Sodium hypochlorite is confirmed in those solutions and thus obtaind products are hardly soluble into organic solvents. On the other hand, when complex salt is put into aqueous sodium hydroxide and sodium carbonate, decreasing of pH and appearance of sodium hypochlorite are scarcely confirmed and a color of filtered solution becomes blue, as is the case within the concentrated (10 wt%) alkaline solution. Thus obtained products are easily soluble in organic solvents such as benzene (see Table4).

Action of aqueous sodium hydroxide toward complex salt is the same as that of DMF, which extracts cupric chloride from the complex salt. Then NaOH is allowed to put into formula (1) in place of DMF. Contrary to this, from the confirmation of sodium hypochorite, the action of alkaline solution toward BTC and double salt may be thought as an extracting reaction of chlorine following appearance of radicals. It is shown in rormula (3).


(3)

The combination at 4 and 4′ may be mainly advanced according to formula (3), but a part of radical generated on the dissociated tetrazonium salt may be combined at another sites besides 4 and 4′, followed by making a side chain or crosslinking, becauae both BTC and double salt are gradually dissolved in water and dissociated.

Polymers insoluble in organic solvents are decomposed by the reduction, subsequently a component soluble in such solvents as benzene and DMF is obtained. Accordingly, the molecular weight of a component insoluble in organic solvents may be large beyond the anticipation constructing a complicated structure. The polymer soluble in DMF is previously obtained by the method of Berlin with 3,3′ dicarboxybenzidin. [1]

Calculation based on 2550 of molecular weigt and 7% of nitrogen content in Table 4 gives m : n = 3 : 2. Then 2/10 of nitrogen may be left behind as azo-group and the constitution of the component is equivalent to (⌬ × 30 + N = N × 6). And the melting point becomes linearly high in accordance with increase of molecular weight.

In case the complex salt was added within ammonia solution diluted with water ten times by volume of 28% concentrated solution, the molecular weight of the fractionated component became 980 and its melting point was 190°C (a low value).

However, when BTC and double salt were added within the same solution, the products were insoluble in organic solvents and their melting points became extremely high. And further, it was assumed that 3/10−1/3 of nitrogen was remained as azogroup because the content of nitrogen became 9.5 — 11.9%.

Action of Cu^+ + NH_4OH toward the materials are almost the same as in case of diluted ammonia solution and the products are soluble in benzene in case of complex salt and insoluble in case of BTC and double salt (see Table 1).

3.4 IR spectrum of the polymer

IR spectrum of the polymers obtained by the action of DMF and aqueous sodium hydroxide toward the materials are shown in Fig. 3. An

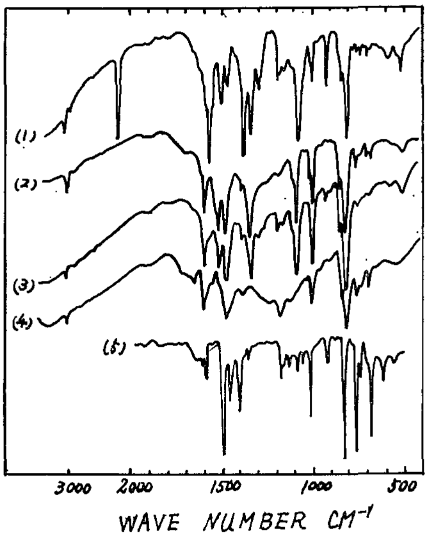


Fig3. IR spectrum of the fractionated comPonent
(1) BTC − Cu_2 Cl_2complex salt
(2) (1) + 10% DMF/Benzene (M=3300)
(3) (1) + 10% NaoHag (M=2550)
(4) BTC + 10% NaOH (insoluble in benzene)
(5) p−Quattraphenyl

absoption of $-N \equiv N$ at 2230cm^{-1} on the complex salt is completely disappeared in the polymer. IR spectrums of complex salt (1) and the polymer (2), (3) made from complex salt have a similar characteristic absorption band at nearly the same wave number of p-Quatraphenyl and especially a strong absorption is observed in all specimen at 810cm^{-1} which is assigned as paraphenyl combination.[5] But that of polymer (4) made from BTC is distinctly different from that of other specimen on a broad absorption band at $1350-1100\mathrm{cm}^{-1}$. Then, the polymer (4) may be consrutcted with a more complicated structnre than that of (2) and (3).

4. Summary

As mentioned above, cupric chloride is extracted from the complex salt by the action of DMF and concentrated sodium hydroxide solution and a pair of radical face to face at the sites of 4 and 4′ of biphenyl group is formed following the instantaneous combination of radicals at 4 and 4′. This polymerization proceeds by the repeating action of appearance and disappearance of radicals with the growth of molecule. Thus obtained products are easily soluble in organic solvents.

Contrary to this, BTC and double salt are scarcely acted on by DMF, but they are polymerized wilhin alkaline solutions by extracting reaction of chlorine following appearance of radicals at the sites of 4 and 4′. In this case, the product is hardly soluble in organic solvents. The reason is that a complicated union besides the sites at 4 and 4′ maybe occurs, unlike the solid-like reaction, when radical is generated a part of dissociated tetrazonium salt by the extracting reaction of chlorine with alkaline solutions, due to the solubility of BTC and double salt.

Comparing these reaction mechantsms, the extraction of cupric chloride toward complex salt is clearly different from the extraction of chlorine toward BTC and double salt. IR spectrums and nitrogen contents are also different each other.

(Part of this study was presented at the 21 th Annual Meeting of the Chemical Society of Japan on March 31, 1968).

The authors wish to thank professor Osamu Ishizuka and Mr. Masao Okamoto for their IR spectral measurement and vauable discussions.

References

1) A. A. Berlin, J. Polymer Sci., **55**. 621 (1961) ; A. A. Berlin, V. I. Liogonkii and V. P. Parini, ibid, **55**, 675 (1961).

2) Lecture of Experimental Chemistry vol. **11**, p. 7, Maruzen, Tokyo (1956); R. K. Murmann, Chemistry of the complex salt, translated by Nakahara and Fujieda, Kyoritsu publish., Tokyo (1966).

3) Handbook ot Chemistry, Fund. vol. 1, p. 96, Maruzen (1966).

4) Lecture of Experimental Chemistry vol .1, P. 190, Maruzen, (1957).

5) J. E. Stewart. et. al. J. Res. Natl. Bur. Std., **60**, 125 (1958); C. S. Marvel, et. al. J. Am. Chem. Soc., **81**, 448 (1959); P. kovacic, et.al., J. Am. Chem. Soc., **85**, 454 (1963).

ベンジジンテトラゾニウム錯塩の DMF および アルカリ液中のラジカル重合

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要　旨

筆者らはベンジジンデトラゾニウムクロライド（BTC）の塩化第1銅による錯塩が，DMF などの有機溶媒および濃厚アルカリ水溶液の作用で重合し，ベンゼン，DMF などに溶け易く，$-(-\langle\bigcirc\rangle-)-_{40}$ の成分を生じることを知った。一方 Berlin は BTC 溶液に $Cu^{+}+NH_4OH$ を加えて，有機溶媒に溶けないポリフエニルを合成している。これと筆者らの方法を比較するために，1) BTC, 2) BTC-Cu_2Cl_2,$ZnCl_2$ 複塩，3) BTC-Cu_2Cl_2 錯塩を単離し，有機および無機の試薬を作用させた。使用液の pH 低下と塩化第2銅および塩素の検出から，錯塩からは塩化第2銅の引抜反応，複塩および BTC からは塩素の引抜反応で重合することが確認された。生成物の分別体は前者が有機溶媒に溶け易く，後者は溶けにくい。赤外分光スペクトルから前者は 4, 4′ 結合が主であり，後者は複雑な構造をとると推定される。